(12) # EUROPEAN PATENT APPLICATION

(21) Application number: **85302813.2**

(22) Date of filing: **23.04.85**

(51) Int. Cl.⁴: **C 10 G 65/00**

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(54) **Catalytic dewaxing of light and heavy oils in dual parallel reactors.**

(57) Relatively heavy or relatively light lube chargestocks are dewaxed in two parallel, separate reactors. The reactor used for dewaxing the relatively light chargestocks contains a crystalline aluminosilicate zeolite such as natural or synthetic ferrierite, ZSM-22, ZSM-23 and ZSM-35 zeolites and/or mixtures thereof. The reactor used for dewaxing the relatively heavy chargestocks contains a crystalline aluminosilicate zeolite such as ZSM-5, ZSM-11 zeolites, ZSM-5/ZSM-11 intermediates and/or mixtures thereof.

CATALYTIC DEWAXING OF LIGHT AND HEAVY OILS
IN DUAL PARALLEL REACTORS

This invention relates to a novel process for dewaxing light and heavy oils in two parallel reactors, each containing a different porous crystalline catalyst.

It is known to treat gas oil fractions, i.e., petroleum fractions having an initial boiling point above 165 C to selectively remove paraffinic hydrocarbons therefrom. This permits many of these fractions to meet a pour point standard. In particular, many light gas oil fractions, that is, those which are used for No. 2 fuel (home heating oil) and/or Diesel fuel, have pour points which are too high to permit their intended use. A typical pour point specification is -18 C (0 F), whereas it is not uncommon for such gas oil fractions to have untreated pour points of 10 C (50 F) or higher.

Hydrocracked and solvent refined lubricating oils generally have an unacceptably high pour point and require dewaxing. Solvent dewaxing is a well-known and effective process, but it is expensive. U.S. Reissue Patent 28,398 describes a catalytic dewaxing process wherein a particular crystalline zeolite is used. To obtain lubricants and specialty oils with outstanding resistance to oxidation, it is often necessary to hydrotreat the oil after catalytic dewaxing, as taught in U.S. Patent 4,137,148. U.S. Patents 4,283,271 and 4,283,272 teach continuous processes for producing dewaxed lubricating oil base stock including hydrocracking a hydrocarbon feedstock, catalytically dewaxing the hydrocrackate and hydrotreating the dewaxed hydrocrackate. Both of the latter patents teach the use of a catalyst comprising zeolite ZSM-5 or ZSM-11 for the dewaxing phase. U.S. Patent 4,259,174 teaches the dewaxing lubricating oil stock over a catalyst comprising synthetic offretite. U.S. Patents 4,222,855, 4,372,839 and 4,414,097 teach catalytic dewaxing of waxy hydrocarbon feedstocks over ZSM-23.

There is a need for processes which can efficiently provide high quality lubricants from interchangeable and readily available low grade crudes.

Accordingly, the present invention provides an integrated process for catalytically dewaxing a relatively light petroleum chargestock, characterized by a 50% boiling point of less than about 454 C (850 F) and a kinematic viscosity at 100 C of less than about 9 centistokes, a relatively heavy petroleum chargestocks, characterized by a 50% boiling point of greater than about 454 C (850 F and kinematic viscosity at 100 C of greater than about 9 centistokes, comprising: dewaxing the relatively light petroleum chargestocks in a first dewaxing reactor means with a dewaxing catalyst of a crystalline aluminosilicate zeolite having pore openings defined by: (1) a ratio of sorption of n-hexane to o-xylene, on a volume percent basis, of greater than about 3, which sorption is determined at a P/P_o of 0.1 and at a temperature of 50 C for n-hexane and 80 C for o-xylene and (2) by the ability of selectively cracking 3-methylpentane (3MP) in preference to the doubly branched 2,3-dimethylbutane (DMB) at 538 C (1000 F) and 1 atmosphere pressure from a 1/1/1 weight ratio mixture of n-hexane/3-methyl-pentane/ 2,3-dimethylbutane, with the ratio of rate constants k_{3MP}/k_{DMB} determined at a temperature of 538 C (1000 F) being in excess of about 2 to produce a catalytically dewaxed light stock, dewaxing the relatively heavy petroleum chargestock in a second dewaxing reactor with a dewaxing catalyst of a crystalline aluminosilicate zeolite having pore openings defined by: (1) a ratio of sorption of n-hexane to o-xylene, on a volume percent basis, of less than about 3, which sorption is determined at a P/P_o of 0.1 and at a temperature of 50 C for n-hexane and 80 C for o-xylene; (2) by the ability of selectively cracking 3-methylpentane (3MP) in preference to the doubly branched 2,3-dimethylbutane (DMB) at 538 C (1000 F) and 1 atmosphere pressure from a 1/1/1 weight ratio mixture of n-hexane/3-methyl-pentane/

2,3-dimethylbutane, with the ratio of the rate constants k_{3MP}/k_{DMB} determined at a temperature of 538 C (1000 F) being less than about 2; and, (3) a Constraint Index value of greater than about 1, to produce a catalytically dewaxed heavy stock passing at least intermitently, said dewaxed light and heavy stocks over a downstream hydrotreating reactor.

In another embodiment, a process for dewaxing a lubricant chargestock comprising material boiling above 454 C and below 454 C over a conventional shape selective catalytic hydrodewaxing catalyst at conventional catalytic hydrodewaxing conditions, followed by conventional hydrotreating of catalytically hydrodewaxed oil over conventional hydrotreating catalyst operated at conventional hydrotreating conditions, the improvement characterized by separating at least a portion of the feed into a relatively heavy fraction characterized by a 50% boiling point of at least 454 C and a relatively light fraction characterized by a 50% boiling point less than 454 C, and subjecting said light fraction to catalytic hydrodewaxing over a catalyst comprising natural and synthetic ferrierites, ZSM-22, ZSM-23, ZSM-35 and mixtures thereof and subjecting said relatively heavy oil fraction to catalytic dewaxing over a catalytic hydrodewaxing catalyst comprising ZSM-5, ZSM-11, ZSM-5/ZSM-11 intermediates and mixtures thereof.

Figure 1 is a schematic representation of a process of the present invention.

Figure 2 is a graphical representation of the dewaxing experiments data of Examples 1 and 2.

Figure 3 is a graphical representation of the dewaxing experiments data of Examples 3 and 4.

The relatively light petroleum chargestock may be obtained from distillation of crudes, and solvent extraction and/or hydrocracking of light distillate cuts, and it is exemplified by light neutrals, transformer oils, refrigerator oils, and specialty oils such as spray oils.

The relatively heavy petroleum chargestock may be obtained from distillation of crudes, and solvent extraction and/or hydrocracking of heavy distillate cuts and residua, and is exemplified by heavy neutrals, and residual propane deasphalted (PD) raffinates.

FEEDSTOCK PROPERTIES

The light oils used herein are typically characterized by a 50% boiling point less than about 454 C (850 F). Preferably, the light oils will have a 50% boiling point within the range of about 315-454 C (600-850 F), and most preferably a 50% boiling point temperature within the range of 371-441 C (700-825 F).

The viscosity of the relatively light oil will usually be less than about 9 centistokes, as measured at 100 C, and many times will be less than 8 centistokes, or even less than 6 centistokes measured at 100 C.

The relatively heavy oil will usually have a 50% boiling point in excess of 454 C (850 F), and frequently will have a 50% boiling point within the range of 482-566 C (900-1050 F), and most preferably within the range of 496-552 C (925-1025 F).

The viscosity of the relatively heavy oil fraction will usually be in excess of 9 centistokes as measured at 100 C, and many times will be in excess of 10 centistokes, or even 20 centistokes, as measured at 100 C.

Both the relatively light and the relatively heavy chargestocks are processed either through the conventional furfural extraction or the hydrocracking process steps prior to their introduction to one of the two dual reactors of the present invention. It is known in the art that the furfural extraction and the hydrocracking steps remove undesired aromatic and heterocyclic components from the chargestock. If the chargestock is processed through the furfural extraction step prior to the introduction thereof into the present process, the furfural raffinate stream comprises the feedstock of the process of the present invention. If

the chargestock is processed through the hydrocracking step prior to the introduction thereof to the present process, the effluent of the hydrocracking step, also known as hydrocrackate, comprises the feedstock of the process of the present invention.

The relatively light chargestock is conducted to a first fixed bed catalytic reactor containing a crystalline aluminosilicate zeolite having pore openings defined by: (1) a ratio of sorption of n-hexane to o-xylene, on a volume percent basis, of greater than 3, which sorption is determined at a P/P_0 of 0.1 and at a temperature of 50 C for n-hexane and 80 C for o-xylene and (2) by the ability of selectively cracking 3-methylpentane (3MP) in preference to the doubly branched 2,3-dimethylbutane (DMB) at 538 C (1000 F) and 1 atmosphere pressure from a 1/1/1 weight ratio mixture of n-hexane/3-methyl-pentane/2,3-dimethylbutane, with the ratio of rate constants k_{3MP}/k_{DMB} determined at 538 C (1000 F) being in excess of about 2. Suitable zeolites used in the first reactor means are exemplified by ferrierite, ZSM-22, ZSM-23 and ZSM-35 zeolites and/or mixtures thereof. The quantities P/P_0 and k_{3MP}/k_{DMB} are defined above.

Ferrierite is a naturally-occurring mineral, described in the literature, see, e.g., D.W. Breck, ZEOLITE MOLECULAR SIEVES, John Wiley and Sons (1974), pages 125-127, 146, 219 and 625, the entire contents of which are incorporated herein by reference.

ZSM-22 is a highly siliceous zeolite which can be prepared from a reaction mixture comprising a source of silica, an alkane diamine, an alkali metal oxide or an alkaline earth metal oxide, e.g., sodium, potassium, cesium, calcium or strontium, water, and alumina, and having a composition, in terms of mole ratios of oxides, falling within the following ratios:

Reactants		Broad	Preferred	Most Preferred
SiO_2/Al_2O_3	=	20 to ∞	30 to 1000	60 to 200
H_2O/SiO_2	=	10 to 100	20 to 60	20 to 60
OH^-/SiO_2	=	0 to 0.3	0.1 to 0.2	0.1 to 0.2
M^+/SiO_2	=	0 to 2.0	0.1 to 1.0	0.1 to 1.0
RN/SiO_2	=	0.01 to 2.0	0.05 to 1.0	0.05 to 1.0

wherein RN is a C_2-C_{12} alkane diamine of the formula $H_2N-(CH_2)_n-NH_2$ (abbreviated C_nDN), n = 2 to 12, and preferably is 5 to 8, and M is an alkali metal or an alkaline earth metal and maintaining the mixture at crystallization temperature until crystals of the ZSM-22 zeolite are formed. Thereafter, the crystals are separated from the liquid by any conventional means, washed and recovered.

Crystallization can be carried out at either static or stirred conditions in a reactor vessel, e.g., a polypropylene jar, teflon lined or stainless steel autoclaves, at 80 C (176 F) to about 210 C (410 F) for about 6 hours to 150 days. Thereafter, the crystals are separated from the liquid and recovered. The composition can be prepared utilizing materials which supply the appropriate oxide. Such materials include aluminates, alumina, silicates, sodium silicate, silica hydrosol, silica gel, silicic acid, sodium, potassium or cesium hydroxide, and an alkane diamine. Suitable diamines are, e.g., ethanediamine, propanediamine, butanediamine, pentanediamine, hexanediamine, heptanediamine, octane-diamine, nonanediamine, decanediamine, undecanediamine, duodecane-diamine. The reaction mixture can be prepared either batchwise or continuously. Crystal size and crystallization time of the crystalline material varies with the nature of the reaction mixture employed and the crystallization conditions.

As set forth above, the ZSM-22 zeolite can be prepared at a relatively wide range of SiO_2/Al_2O_3 ratios of about 20 to about infinity (∞). However, it has been found that larger alkali

metal cations, e.g., K^+ and Cs^+, are preferably used at the SiO_2/Al_2O_3 ratios of about 20 to about 90 to obtain ZSM-22 crystals substantially free of impurities or other zeolites. The potassium (K^+) cation is preferred at such low SiO_2/Al_2O_3 ratios because cesium (Cs) appears to decrease the reaction rate. At the SiO_2/Al_2O_3 ratios of 90 or above, e.g., 90 to 200, smaller cations, e.g., sodium (Na^+) cations, are preferably used to produce substantially 100% crystalline ZSM-22.

The highly siliceous ZSM-22 zeolite comprises crystalline, three-dimensional continuous framework silicon-containing structures or crystals which result when all the oxygen atoms in the tetrahedra are mutually shared between tetrahedral atoms of silicon or aluminum, and which can exist with a network of mostly SiO_2, i.e., exclusive of any intracrystalline cations. In the as-synthesized form, the ZSM-22 has a calculated composition, in terms of moles of oxides, after dehydration, per 100 moles of silica, as follows:

$$(0.02 \text{ to } 10)RN:(0 \text{ to } 2)M_{2/n}O:(0 \text{ to } 5)Al_2O_3:100SiO_2$$
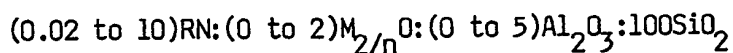
wherein RN is a C_2-C_{12} alkane diamine and M is an alkali metal or an alkaline earth metal having a valence n, e.g., Na, K, Cs, Li, Ca or Sr.

ZSM-22 can further be identified by its sorptive characteristics and its X-ray diffraction pattern. The original cations of the as-synthesized ZSM-22 may be replaced at least in part by other ions using conventional ion exchange techniques. It may be necessary to precalcine the ZSM-22 zeolite crystals prior to ion exchange. The replacing ions introduced to replace the original alkali, alkaline earth and/or organic cations may be any ions that are desired so long as they can pass through the channels within the zeolite crystals. Desired replacing ions are those of hydrogen, rare earth metals, metals of Groups IB, IIA, IIB, IIIA, IIIB, IVA, IVB, VIB and VIII of the Periodic Table. Among the metals, those

particularly preferred are rare earth metals, manganese, zinc and those of Group VIII of the Periodic Table.

ZSM-22 zeolite described herein has a definite X-ray diffraction pattern, set forth below in Table A, which distinguishes it from other crystalline materials.

TABLE A

Most Significant Lines of ZSM-22

Interplanar d-spacings (Å)	Relative Intensity
10.9 ± 0.2	M-VS
8.7 ± 0.16	W
6.94 ± 0.10	W-M
5.40 ± 0.08	W
4.58 ± 0.07	W
4.36 ± 0.07	VS
3.68 ± 0.05	VS
3.62 ± 0.05	S-VS
3.47 ± 0.04	M-S
3.30 ± 0.04	W
2.74 ± 0.02	W
2.52 ± 0.02	W

These values were determined by standard techniques. The radiation was the K-alpha doublet of copper and a diffractometer equipped with a scintillation counter and an associated computer were used. The peak heights, I, and the positions as a function of 2 theta, where theta is the Bragg angle, were determined using algorithms on the computer associated with the spectrometer. From these, the relative intensities, $100 \ I/I_o$, where I_o is the intensity of the strongest line or peak, and d (obs.) the interplanar spacing in angstroms (Å), corresponding to the recorded lines, were determined. In Table I, the relative intensities are given in terms of the following symbols vs = very strong, s =

strong, m = medium, w = weak, etc. It should be understood that
this X-ray diffraction pattern is characteristic of all the species
of ZSM-22 zeolite compositions. Ion exchange of the alkali or
alkaline earth metal cations with other ions results in a zeolite
which reveals substantially the same X-ray diffraction pattern as
that of Table I with some minor shifts in interplanar spacing and
variations in relative intensity. Other minor variations can occur,
depending on the silica to alumina ratio of the particular sample,
as well as its degree of thermal treatment.

The ZSM-22 zeolite freely sorbs normal hexane and has a
pore dimension greater than about 4 Angstroms. In addition, the
structure of the zeolite must provide constrained access to larger
molecules. It is sometimes possible to judge from a known crystal
structure whether such constrained access exists. For example, if
the only pore windows in a crystal are formed by 8-membered rings of
silicon and aluminum atoms, then access by molecules of larger
cross-section than normal hexane is excluded and the zeolite is not
of the desired type. Windows of 10-membered rings are preferred,
although, in some instances, excessive puckering or pore blockage
may render these zeolites ineffective. Twelve-membered rings do not
generally appear to offer sufficient constraint to produce the
advantageous hydrocarbon conversions, although puckered structures
exist such as TMA offretite which is a known effective zeolite.
Also, such twelve-membered structures can be conceived that may be
operative due to pore blockage or other causes.

Rather than attempt to judge from crystal structure whether
or not a zeolite possesses the necessary constrained access, a
simple determination of the "constraint index" may be made by
passing continuously a mixture of an equal weight of normal hexane
and 3-methylpentane over a sample of zeolite at atmospheric pressure
according to the following procedure. A sample of the zeolite, in
the form of pellets or extrudate, is crushed to a particle size
about that of coarse sand and mounted in a glass tube. Prior to

testing, the zeolite is treated with a stream of air at 538 C (1000 F) for at least 15 minutes. The zeolite is then flushed with helium and the temperature adjusted to between 550 F (288 C) and 950 F (510 C) to give an overall conversion between 10% and 60%. The mixture of hydrocarbons is passed at a 1 liquid hourly space velocity (LHSV), i.e., 1 volume of liquid hydrocarbon per volume of zeolite per hour, over the zeolite with a helium dilution to give a helium to total hydrocarbon mole ratio of 4:1. After 20 minutes on stream, a sample of the effluent is taken and analyzed, most conveniently by gas chromatography, to determine the fraction remaining unchanged for each of the two hydrocarbons.

The "constraint index" is calculated as follows:

$$\text{Constraint Index} = \frac{\log_{10} (\text{fraction of n-hexane remaining})}{\log_{10} (\text{fraction of 3-methylpentane remaining})}$$

The constraint index approximates the ratio of the cracking rate constants for the two hydrocarbons. The ZSM-22 zeolite has a constraint index of about 7.3 at 800 F (427 C). Constraint Index (CI) values for some other typical zeolites are:

Zeolite	C.I.
ZSM-5	8.3
ZSM-11	8.7
ZSM-12	2
ZSM-23	9.1
ZSM-38	2
ZSM-35	4.5
Clinoptilolite	3.4
TMA Offretite	3.7
Beta	0.6
ZSM-4	0.5
H-Zeolon	0.4
REY	0.4
Amorphous Silica-Alumina (non-zeolite)	0.6
Erionite	38

It is to be realized that the above constraint index values
typically characterize the specified zeolites but that these are the
cumulative result of several variables used in determination and
calculation thereof. Thus, for a given zeolite depending on the
temperature employed within the aforenoted range of 288 to 510 F,
with accompanying conversion between 10% and 60%, the constraint
index may vary within the indicated approximate range of 1 to 12.
Likewise, other variables, such as the crystal size of the zeolite,
the presence of possible occluded contaminants and binders
intimately combined with the zeolite, may affect the constraint
index. The constraint index is a useful means for characterizing
zeolites, but it is an approximation.

It may occasionally be necessary to use somewhat more
severe conditions for samples of very low activity, such as those
having a very high silica to alumina mole ratio. In those
instances, a temperature of up to about 540 C and a liquid hourly

space velocity of less than one, such as 0.1 or less, can be
employed in order to achieve a minimum total conversion of about 10%.

The sorption of hydrocarbons by ZSM-22 has been surveyed
and the results are summarized in Table B. Sorption capacities for
n-hexane (normal hexane), cyclohexane, and water are about 4% by
weight, or about one third that of ZSM-5. Cyclohexane and o-xylene
sorption is relatively slow, making it difficult to determine
equilibrium capacities.

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TABLE B

ZSM-22 Sorption Data

| | | | | Sorptions (wt %)[a] | | |
| | | | 3-methyl- | Cyclo- | | |
Sample	Form	n-hexane	pentane	hexane[c]	H_2O	o-xylene[b]
1	Hydrogen	3.9	-	2.8	-	-
2	Hydrogen	4.2	3.9	1.1	-	2
3	Hydrogen	4.1	-	3.3	4.7	-
4	as-synthesized	3.4	-	-	-	-

a. Hydrocarbons: vapor pressure = 20mm Hg, temperature = 25 C;
       water-pressure = 12mm Hg, temperature = 25 C.
b. vapor pressure = 3.7mm Hg, temperature = 120 C.
c. slow tailing sorption, nonequilibrium values.

The n-hexane/o-xylene ratios may vary under different conditions,

as illustrated by the data of Table C, below:

TABLE C

Additional Adsorption Properties of ZSM-22

Sample Temperature = 100 C

Sample	Form	Sorbate	Vapor Pressure (mm Hg)	P/P_0	Wt % sorbed
5	Hydrogen	n-Hexane	80	0.04	4.0
6	Hydrogen	o-Xylene	5	0.025	1.1

The ZSM-22 zeolite, as synthesized, tends to crystallize as
agglomerates of elongated crystals having the size of about 0.5 to
about 2.0 microns (μ). Ballmilling fractures these crystals into
smaller size crystallites (about 0.1 μ) without significant loss of
crystallinity. The zeolite can be shaped into a wide variety of
particle sizes. Generally speaking, the particles can be in the

form of a powder, a granule, or a molded product, such as an
extrudate having particle size of 10 mm to 0.4 microns. In cases
where the catalyst is molded, such as by extrusion, the crystals can
be extruded before drying or partially dried and then extruded.

ZSM-23 is described in U.S. Patents 4,076,842 and 4,104,151.

ZSM-35 is a synthetic analogue of ferrierite, and it is
described in U.S. Patents 4,016,245 and 4,107,195.

The relatively heavy chargestock is conducted to a second
fixed catalytic reactor containing a crystalline aluminosilicate
zeolite having pore openings defined by: (1) a ratio of sorption of
n-hexane to o-xylene, on a volume percent basis, of less than about
3, which sorption is determined at a P/P_0 of 0.1 and at a
temperature of 50 C for n-hexane and 80 C for o-xylene; and (2) the
ability of selectively cracking 3-methylpentane (3MP) in preference
to the doubly branched 2,3-dimethylbutane (DMB) at 538 F (1000 F)
and 1 atmosphere pressure from a 1/1/1 weight ratio mixture of
n-hexane/3-methyl-pentane/2,3-dimethylbutane, with the ratio of rate
constants k_{3MP}/k_{DMB} determined at a temperature of 538 C (1000
F) being less than about 2; and (3) a Constraint Index value of
greater than about 1. The zeolite contained in the second reactor
is exemplified by ZSM-5, ZSM-11, ZSM-5/ZSM-11 intermediates and/or
mixtures thereof.

ZSM-5 having a silica:alumina (SiO_2:Al_2O_3) mole ratio
of at least 5 is described in U.S. Patent 3,702,886.

ZSM-5 having a SiO_2:Al_2O_3 mole ratio of at least 200
is described in U.S. Patent Re. 29,948.

ZSM-11 is described in U.S. Patent 3,709,979.

ZSM-5/ZSM-11 intermediates are described in U.S. Patent
4,229,424.

The catalysts in the first and the second fixed bed
catalytic reactors may be used without a metal component. In the
preferred embodiment, however, the catalysts contain a metal
hydrogenation component, i.e., about 0.05 to about 2% by weight of a

metal, metal oxide or metal sulfide from Group VIIIA of the Periodic
Chart of the Elements (published by the Fischer Scientific Company,
Catalog Number 5-702-10) or a mixture thereof, alone or in
combination with about 0.1% to about 10% by weight of one or more
metal, metal oxide or metal sulfide from Group VIA of the Periodic
Chart of the Elements. Examples of the metals from Group VIIIA are
platinum, palladium, irridium, ruthenium, cobalt and nickel.
Examples of the metals from Group VIA are chromium, molybdenum and
tungsten. In the most preferred embodiment, ZSM-23 zeolite
comprising about 0.05 to about 2.0% by weight of platinum is used in
the first dewaxing catalytic reactor, and ZSM-5 zeolite comprising
about 0.5 to about 5.0% by weight of nickel is used in the second
dewaxing catalytic reactor. Both dewaxing reactors are operated at
a temperature of 200 to 500 C, preferably at 285 to 400 C, at
pressure of 450 to 21,000 kPa (50 to 3000 psig), preferably about
3,500 to 10,500 kPa (500 to 1500 psig), and at about 0.1 to about 10
liquid hourly space velocity (LHSV), preferably about 0.5 to about 2
LHSV, and, when hydrogen is used, 90 to 1,800 volumes of H_2 at
standard conditions per volume of liquid at standard conditions, V/V
(500 to 10,000 standard cubic feet of hydrogen per barrel of feed,
SCFB), preferably 180 to 900 V/V (1000 to 5000 SCFB). The severity
in the dewaxing reactors is such that the effluents of the reactors
have the desired pour point.

The effluent from the first or the second catalytic
dewaxing reactor is conducted to a common hydrotreating unit
operated in the same broad range of conditions used in the two
catalytic, dewaxing reactors, but preferably at a lower temperature,
usually 200 to 315 C. The hydrotreating unit contains a
conventional hydrotreating catalyst, such as one or more metals from
Group VIIIA (e.g., cobalt and nickel) and one or more metals from
Group VIA (e.g., molybdenum and tungsten) of the Periodic Chart of
the Elements, supported by an inorganic oxide, such as alumina or
silica-alumina. Examples of some specific hydrotreating catalysts

are cobalt-molybdate or nickel-molybdate on an alumina support.

The effluent from the hydrotreating unit is passed to a conventional separation section wherein light hydrocarbons and hydrogen are separated from the stabilized dewaxed lubricating oil stock.

The invention will now be described in connection with one exemplary embodiment thereof shown in Figure 1.

The relatively light chargestock is introduced through a line 2 into a first reactor 5 containing a crystalline aluminosilicate zeolite of the first type, as defined above, such as ferrierite, ZSM-22, ZSM-23 or ZSM-35 zeolite catalysts wherein the chargestock is subjected to dewaxing conditions. Alternately, a relatively heavy chargestock is conducted through a conduit 4 into a second reactor 12 containing a crystalline aluminosilicate zeolite of the second type, defined above, such as ZSM-5, ZSM-11 or ZSM-5/ZSM-11 intermediates zeolite catalysts, wherein it also is subjected to dewaxing conditions.

When reactor 5 is operating, reactor 12 is regenerating. When reactor 12 is operating, reactor 5 is regenerating. The process will be described with the reactor 5 operating and reactor 12 being regenerated.

The effluent of the reactor 5 is conducted via conduits 15 and 16 to hydrotreater 17. Hydrotreater 17 contains a hydrotreating catalyst and operates at hydrotreating conditions. Examples of suitable hydrotreating catalysts include one or more metals from Group VIIIA and one or more metals from Group VIA on alumina or silica-alumina.

The effluent from the hydrotreater is passed via line 18 to high pressure separator 10, wherein it is treated to separate a vapor fraction comprising light hydrocarbons which are removed together with a hydrogen bleed through a line 11 from a liquid fraction comprising a stabilized and dewaxed lubricating oil stock, recovered via line 19. The liquid fraction is passed through line

19 to a separate unit, not shown for recovery of the lubricating oil stock. A portion of the vapor fraction is removed via line 20 to a compressor 21 and then passed through a line 3 to an upstream processing unit, such as a hydrocracker unit, not shown.

Optionally, fresh hydrogen and/or recycle hydrogen streams may be introduced into the reactors 5 and 12 through the conduits 22 and 24, respectively. If hydrogen is not introduced into the reactors 5 and 12, fresh or recycle hydrogen is introduced through a conduit 26 into the hydrotreater 17.

The dewaxing catalysts used in reactors 5 and 12 may be incorporated with a matrix or binder component comprising a material resistant to the temperature and other process conditions.

Useful matrix materials include both synthetic and naturally occurring substances, as well as inorganic materials such as clay, silica and/or metal oxides. The latter may be either naturally occurring or in the form of gelatinous precipitates or gels including mixtures of silica and metal oxides. Naturally occurring clays which can be composited with the zeolite include those of the montmorillonite and kaolin families, which families include the sub-bentonites and the kaolins commonly known as Dixie, McNamee, Georgia and Florida clays or others in which the main mineral constituent is halloysite, kaolinite, dickite, nacrite or anauxite. Such clays can be used in the raw state as originally mined or initially subjected to calcination, acid treatment or chemical modification.

In addition to the foregoing materials, the catalysts employed in reactors 5 and 12 may be composited with a porous matrix material, such as alumina, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania as well as ternary compositions such as silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia and silica-magnesia-ziconia. The matrix can be in the form of a cogel.

The relative proportions of the catalyst component and inorganic oxide gel matrix on the anhydrous basis, may vary widely with the catalyst content ranging from between about 1 to about 99 percent by weight and more usually in the range of about 5 to about 80 percent by weight of the dry composite.

The hydrogenation component associated with the dewaxing catalyst may be on the zeolite component as above-noted or on the matrix component or both.

EXAMPLE 1

Dewaxing Heavy Stock Over ZSM-23

There were two catalysts used in this example: ZSM-23 zeolite containing 0.3 and 1.7 wt.% platinum (Pt). The ZSM-23 zeolite was synthesized as described in U.S. Patent 4,076,842 with pyrrolidine as the source of nitrogen containing cation. It was mixed with 35 wt.% alumina, extruded and impregnated with platinum ammine chloride so that the finished catalyst contained 0.3 wt.% and 1.7 wt% Pt, respectively.

The two heavy charge stocks were a heavy neutral raffinate (from furfural extraction) and a waxy raffinate (from propane deasphalting of residuum followed by furfural extraction), having the following properties:

	Heavy Neutral	Waxy Raffinate
Gravity, API	30.4	25.3
Specific	0.8740	0.9024
Pour Point, F	>115	>115
(K.V. @100 C, cs)	9.91	27.16
Sulfur, wt.%	0.80	1.24
Nitrogen	0.005	0.027
Distillation, F/ C		
IBP	678/359	875/468
5%	851/455	919/493
10%	870/466	940/504
30%	885/474	996/536
50%	908/487	1039/559
70%	925/496	1089/587
90%	950/510	--
95%	960/516	--

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These two chargestocks were passed over the two catalysts at 2,900 kPa (400 psig), 1 LHSV, and 450 V/V (2500 SCFB) H_2 with the results summarized in Table II, below.

TABLE II

Catalyst	Heavy Neutral					Waxy Raffinate	
	0.3% Pt/ZSM-23		1.7% Pt/ZSM-23			0.3% Pt/ZSM-23	
Run No.	1	2	3	4	5	6	7
Cat. Temp., F/	600	653	551	600	651	650	701
C	316	345	288	316	344	343	372
Mat. Bal. Time, Hrs.	18	22 1/2	16 1/2	22 1/2	22 1/2	20	22 1/2
Time on stream, Days	0.8	1.7	1.6	2.5	3.4	2.5	3.4
Mat. Bal., wt.%	99.5	100.3	100.1	--	99.8	100.5	101.5
343 C+(650 F+ Product:							
Yield, wt.%	91.0	87.8	96.2	--	86.7	92.9	96.1
Gravity, API	28.7	28.5	28.7	28.5	29.9	28.3	26.6
g/cc	0.88	0.88	0.88	0.88	0.88	0.89	0.90
Pour Point, F	+45	+50	+85	+45	+50	+60	+75
C	7	10	29	7	10	16	24
Kinematic viscosity:							
K.V. @40 C, cs	87.39	87.90	82.66	88.68	87.68	333.1	379.5
K.V. @100 C, cs	10.38	10.41	10.04	10.51	10.51	25.32	26.31
Viscosity Index	100.1	99.5	101.2	100.3	100.3	98.6	92.9

The results show that target pour point of -12 to -7 C (10-20 F) was not attained even at the dewaxing temperatures of 345-372 C.

EXAMPLE 2

Dewaxing of Heavy Stocks Over ZSM-5

Two chargestocks, having essentially the same properties as those used in Example I, were passed over a ZSM-5 zeolite. The ZSM-5 zeolite had a $SiO_2:Al_2O_3$ mole ratio of 70, it contained

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1% by weight of nickel (Ni), was composited with 35% alumina binder, and was then steamed for about 6 hours at 482 C (900 F) at atmospheric pressure. The chargestocks were contacted with the ZSM-5 zeolite, operating at the same pressure and with the same amount of hydrogen, with the following results:

	Heavy Neutral			Waxy Raffinate	
Run No.	8	9	10	11	12
Liquid Hourly Space Velocity (LHSV)	1.0	1.0	1.0	0.8	0.8
Cat. Temp., F	551	561	558	550	550
C	288	294	292	288	288
Mat. Bal. TIme, Hrs.	18	22*	22.5	20.5	23
Time on stream, Days	0.9	1.9	4.9	0.9	1.8
Mat. Bal., wt.%	94.4	96.0	96.4	98.8	100.7

*At conclusion of material balance, 100 ppm n-methyl pyrrolidone was added to the chargestock.

	Heavy Neutral			Waxy Raffinate	
343 C$^+$ (650 F$^+$) Lube Product					
Yield, wt.%	82.8	81.5	83.3	90.6	90.2
Gravity, API	28.5	27.3	28.0	24.6	24.5
g/cc	0.88	0.89	0.89	0.91	0.91
Pour Point, F	+10	+5	+10	0	+15
C	-12	-15	-12	-18	-9
K.V. @40 C, cs	109.0	108.7	103.8	469.6	471.9
K.V. @100 C, cs	11.42	11.36	11.19	30.22	30.55
Viscosity Index	90.0	89.3	92.4	93.0	93.9

This example shows that ZSM-5 zeolite readily hydrodewaxes these two heavy chargestocks, in contrast to ZSM-23 zeolite which, as Example 1 above illustrates, is not an effective dewaxing catalyst for heavy chargestocks.

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EXAMPLE 3
Dewaxing Light Stock Over ZSM-23

The chargestock was a light neutral furfural extracted raffinate, having the following properties.

Gravity, API	32.1
Specific	0.8649
Pour Point, F/ C	+95/35
K.V. @100 C, cs	4.47
Sulfur, wt.%	0.70
Nitrogen, wt.%	0.003
Distillation, F/ C	
IBP	~ 650/343
5%	681/361
10%	715/379
30%	769/409
50%	804/429
70%	842/450
90%	925/496
95%	968/520

This stock was passed over the two Pt/ZSM-23 catalysts of Example 1 at the same pressure and with the same hydrogen circulation, with the following results:

Catalyst	0.3% Pt/ZSM-23		1.7% Pt/ZSM-23		
Run No.	13	14	15	16	17
Cat. Temp., F	600	650	601	575	625
C	316	343	316	302	329
Mat. Bal. Time, Hrs.	22 1/2	22 1/2	20 1/2	94	22 1/2
Time on stream, Days	4.5	5.4	8.2	12.1	13.0
Mat. Bal., wt.%	102.0	97.3	100.3	100.3	101.2
343 C+ (650 F+) Lube Product					
Yield, wt.%	84.6	78.7	82.5	94.4	86.5
Gravity, API	31.2	30.3	30.3	31.3	30.8
g/cc	0.87	0.87	0.87	0.87	0.87
Pour Point, F	+50	+10	-5	+40	+10
C	10	-12	-21	4	-12
K.V. @40 C, cs	27.34	30.21	33.14	--	30.05
K.V. @100 C, cs	4.96	5.17	5.39	4.95	5.17
Viscosity Index	105.5	99.2	94.1	--	100.6

This example shows that the ZSM-23 zeolite readily hydrodewaxes the light neutral stock.

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EXAMPLE 4

Dewaxing of Light Stock Over ZSM-5

The chargestock of Example 3 was passed over a sample of the ZSM-5 zeolite identified in Example 2 catalyst at the same conditions as in Example 3 with the following results:

Run No.	18	19
Cat. Temp., F/ C	550/288	576/302
Mat. Bal. Time, Hrs.	18	21
Time on Stream, Days	0.8	1.6
Mat. Bal. wt.%	99.4	99.7

610 F$^+$ Lube Product

Yield, wt.%	82.3	76.0
Gravity, API/g/cc	30.0/0.88	28.9/0.88
Pour Point, F/ C	+40/4	+15/-9
K.V. @40 C, cs	29.59	32.93
K.V. @100 C, cs	5.12	5.34
Viscosity Index	100.4	92.1

This Example shows that ZSM-5 zeolite is unexpectedly much less selective as compared to ZSM-23 zeolite for hydrodewaxing the light neutral chargestock, since it produces a product oil of lower viscosity index (V.I.) at the same pour point and at a lower yield than the ZSM-23 zeolite.

Figures 2 and 3 graphically illustrate the results of the dewaxing experiments of Examples 1-4.

As illustrated in Examples 1-4, zeolites having pore openings defined by: (1) ratio of sorption of n-hexane to o-xylene of greater than about 3, and (2) the ratio k_{3MP}/k_{DMB} of greater than about 2, such as zeolite ZSM-23, are surprisingly more selective than zeolites of the second types, such as ZSM-5, for hydrodewaxing light neutral and lower molecular weight waxy lube stocks, giving a higher yield of a higher viscosity index lube oil (Figure 3). The activity of such zeolites, however, is insufficient

to dewax heavy neutral and higher molecular weight chargestocks to
reach target pour points under standard catalytic lube dewaxing
conditions (Figure 2).

In contrast, zeolites of the second type, having pore
openings defined by: (1) a ratio of sorption of n-hexane to o-xylene
of less than about 3; (2) the ratio of k_{3MP}/k_{DMB} of less than
about 2; and (3) Constraint Index of greater than about 1, such as
ZSM-5 zeolite, are surprisingly more selective when they are used to
dewax the heavier chargestocks than the lighter chargestocks, as
measured by yield and viscosity index (Figure 2). The present
process takes advantage of the unexpected selectivity differences of
these two types of zeolites by providing two separate reactors for
catalytically dewaxing relatively light and relatively heavy
chargestocks, respectively.

Although reactors 5 and 12 are described in the drawing as
operating in alternating fashion, i.e. with one reactor idle while
the other is in service, it is also possible to operate with both
reactors in service at the same time.

In this mode of operation, one or more fractionators, not
shown, could be used to provide a relatively light chargestock to
reactor 5 via line 2, and a relatively heavy chargestock via line 4
to reactor 12. Both reactors could operate at the same pressure,
although it is not essential to do this. The reactor effluent may
be mixed and passed directly to hydrotreater 17, or alternatively a
vapor liquid separation means, not shown, may be used to provide a
relatively heavy liquid stream which would be charged via line 16 to
hydrotreater 17. Because the light and heavy fractions would be
mixed together going through the hydrotreater, their must be a means
provided downstream of the hydrotreater to separate these light and
heavy fractions, assuming that such separation is desired. To
accomplish this, conventional distillation columns may be provided
downstream of the high pressure separator 10, which would
fractionate the dewaxed and hydrotreated liquid removed from

separator 10 via line 19 into light and heavy fractions.

Operating with reactors 5 and 12 both in service at the same time may require some additional capital and operating expense due to downstream fracionation, however, this will largely be offset by a savings in upstream fractionation costs. It is not critical to make a good split between light and heavy components upstream of reactors 5 and 12, because a relatively rough separation into light and heavy components will be enough. A better split between light and heavy components can be accomplished in downstream fractionation facilities.

CLAIMS:

1.   An integrated process for catalytically dewaxing a
relatively light petroleum chargestock, characterized by a 50%
boiling point of less than 454 C (850 F) and a kinematic viscosity
at 100 C of less than 9 centistokes, and a relatively heavy
petroleum chargestock, characterized by a 50% boiling point of
greater than 454 C (850 F and kinematic viscosity at 100 C of
greater than 9 centistokes, comprising:

dewaxing the relatively light petroleum chargestock in a
first dewaxing reactor with a dewaxing catalyst of a crystalline
aluminosilicate zeolite having pore openings defined by: (1) a ratio
of sorption of n-hexane to o-xylene, on a volume percent basis, of
greater than 3, which sorption is determined at a P/P_0 of 0.1 and
at a temperature of 50 C for n-hexane and 80 C for o-xylene and (2)
by the ability of selectively cracking 3-methylpentane (3MP) in
preference to the doubly branched 2,3-dimethylbutane (DMB) at 538 C
(1000 F) and 1 atmosphere pressure from a 1/1/1 weight ratio mixture
of n-hexane/3-methyl-pentane/ 2,3-dimethylbutane, with the ratio of
rate constants k_{3MP}/k_{DMB} determined at a temperature of 538 C
(1000 F) being in excess of 2 to produce a catalytically dewaxed
light stock,

dewaxing the relatively heavy petroleum chargestock in a
second dewaxing reactor with a dewaxing catalyst of a crystalline
aluminosilicate zeolite having pore openings defined by: (1) a ratio
of sorption of n-hexane to o-xylene, on a volume percent basis, of
less than 3, which sorption is determined at a P/P_0 of 0.1 and at
a temperature of 50 C for n-hexane and 80 C for o-xylene; (2) by the
ability of selectively cracking 3-methylpentane (3MP) in preference
to the doubly branched 2,3-dimethylbutane (DMB) at 538 C (1000 F)
and 1 atmosphere pressure from a 1/1/1 weight ratio mixture of
n-hexane/3-methyl-pentane/2,3-dimethylbutane, with the ratio of rate

constants k_{3MP}/k_{DMB} determined at a temperature of 538 C (1000 F) being less than 2; and, (3) a Constraint Index value of greater than 1, to produce a catalytically hydrotreated and dewaxed heavy stock bypassing at least intermittently, said dewaxed light and heavy stocks over a downstream hydrotreating reactor.

2. The process of Claim 1 wherein the zeolite in the first dewaxing reactor is selected from the group of natural and synthetic ferrierites, ZSM-22, ZSM-23, ZSM-35 zeolites and mixtures thereof.

3. The process of claim 1 wherein the zeolite in the second dewaxing reactor is selected from the group of ZSM-5, ZSM-11 zeolites, ZSM-5/ZSM-11 intermediates and mixtures thereof.

4. The process of claim 1 wherein both dewaxing reactors operate simultaneously, and wherein the catalytically dewaxed light and heavy stocks are comingled and continuously charged to the hydrotreater.

5. The process of claim 1 wherein only one dewaxing reactor is in service at any time.

6. The process of claim 1 wherein the first dewaxing reactor operates at a temperature of 200 to 500 C, a pressure of 450 to 21,000 kPa, a liquid hourly space velocity of 0.1 to 10 and wherein hydrogen is present in the amount of 90 to 1,800 volume of H_2 per volume of oil, at standard conditions.

7. The process of claim 1 wherein the second dewaxing reactor operates at a temperature of 200 to 500 C, a pressure of 450 to 21,000 kPa, a liquid hourly space velocity of 0.1 to 10 and wherein hydrogen is present in the amount of 90 to 1,800 volume of H_2 per volume of oil, at standard conditions.

8. The process of claim 1 wherein the hydrotreating reactor operates at a temperature of 200 to 316 C a pressure of 450 to 21,000 kPa, a liquid hourly space velocity of 0.1 to 10 and a hydrogen circulation rate of 90 to 1,800 volume of H_2 per volume of oil, at standard conditions.

9.   In a process for dewaxing a lubricant chargestock
comprising material boiling above 454 C and below 454 C over a
conventional shape selective catalytic hydrodewaxing catalyst at
conventional catalytic hydrodewaxing conditions, followed by
conventional hydrotreating of catalytically hydrodewaxed oil over
conventional hydrotreating catalyst operated at conventional
hydrotreating conditions, the improvement characterized by
separating at least a portion of the feed into a relatively heavy
fraction characterized by a 50% boiling point of at least 454 C and
a relatively light fraction characterized by a 50% boiling point
less than 454 C, and subjecting said light fraction to catalytic
hydrodewaxing over a catalyst comprising natural and synthetic
ferrierites, ZSM-22, ZSM-23, ZSM-35 and mixtures thereof and
subjecting said relatively heavy oil fraction to catalytic dewaxing
over a catalytic hydrodewaxing catalyst comprising ZSM-5, ZSM-11,
ZSM-5/ZSM-11 intermediates and mixtures thereof.

10.   The improved process of claim 9 further characterized
in that dewaxing of light and heavy stocks occurs simultaneously in
separate reactors, and the catalytically hydrodewaxed oil is
comingled prior to hydrotreating.

11.   Process of claim 9 wherein catalytic hydrodewaxing of
light and heavy oils occurs sequentially whereby only one of the
catalytic hydrodewaxing reactors is in service at any time.

12.   Process of claim 9 wherein said relatively light oil
has a 50% boiling point of 315-454 C and said heavy oil has a 50%
boiling point within the range of 482-566 C.

13.   Process of claim 9 wherein the light oil has a
viscosity less than 9 centistokes as measured at 100 C, and the
heavy oil has a viscosity in excess of 10 centistokes as measured at
100 C.

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FIG.1

FIG.2

○ ZSM-23 ZEOLITE
  (EXAMPLE I)
● ZSM-5 ZEOLITE
  (EXAMPLE 2)
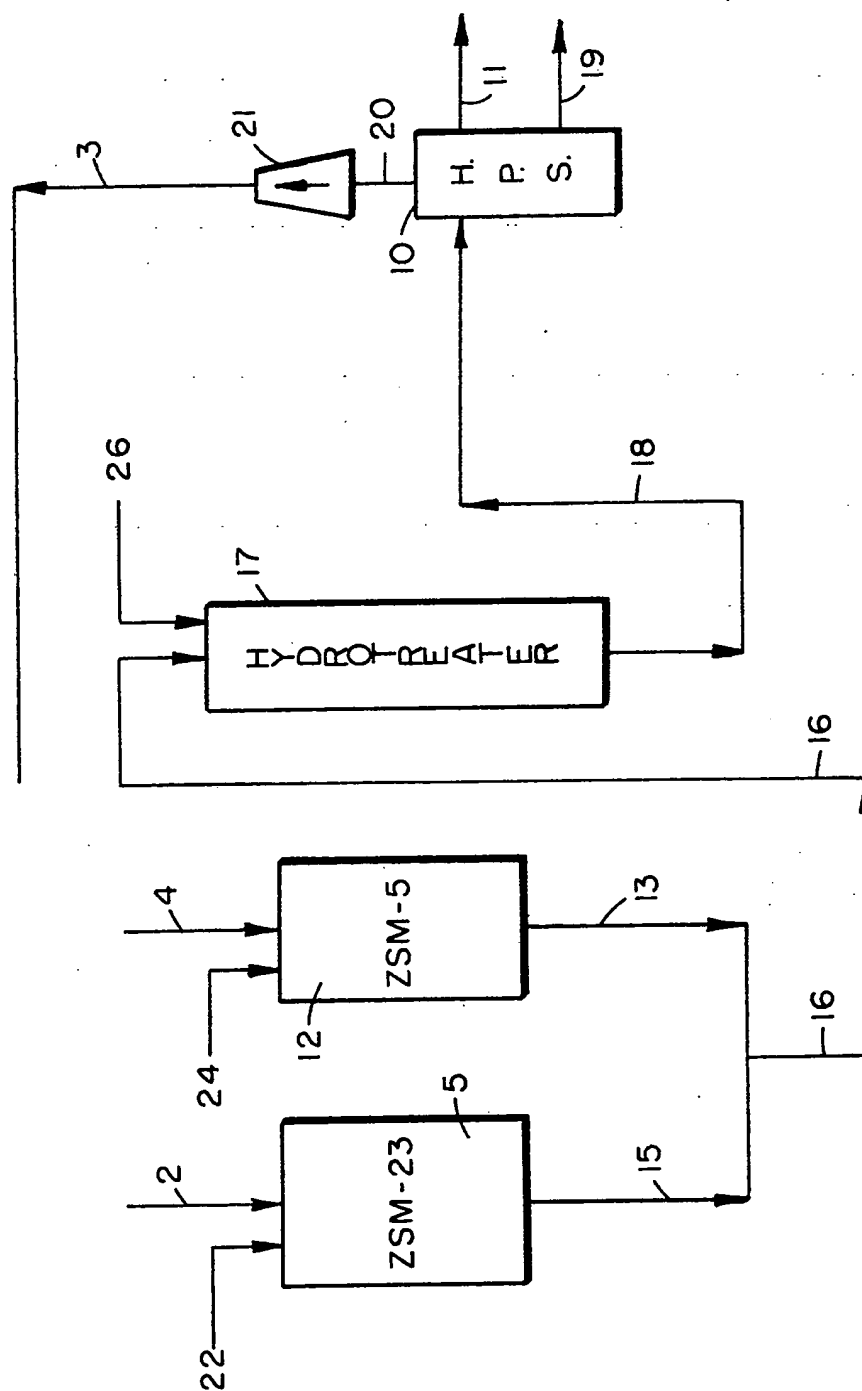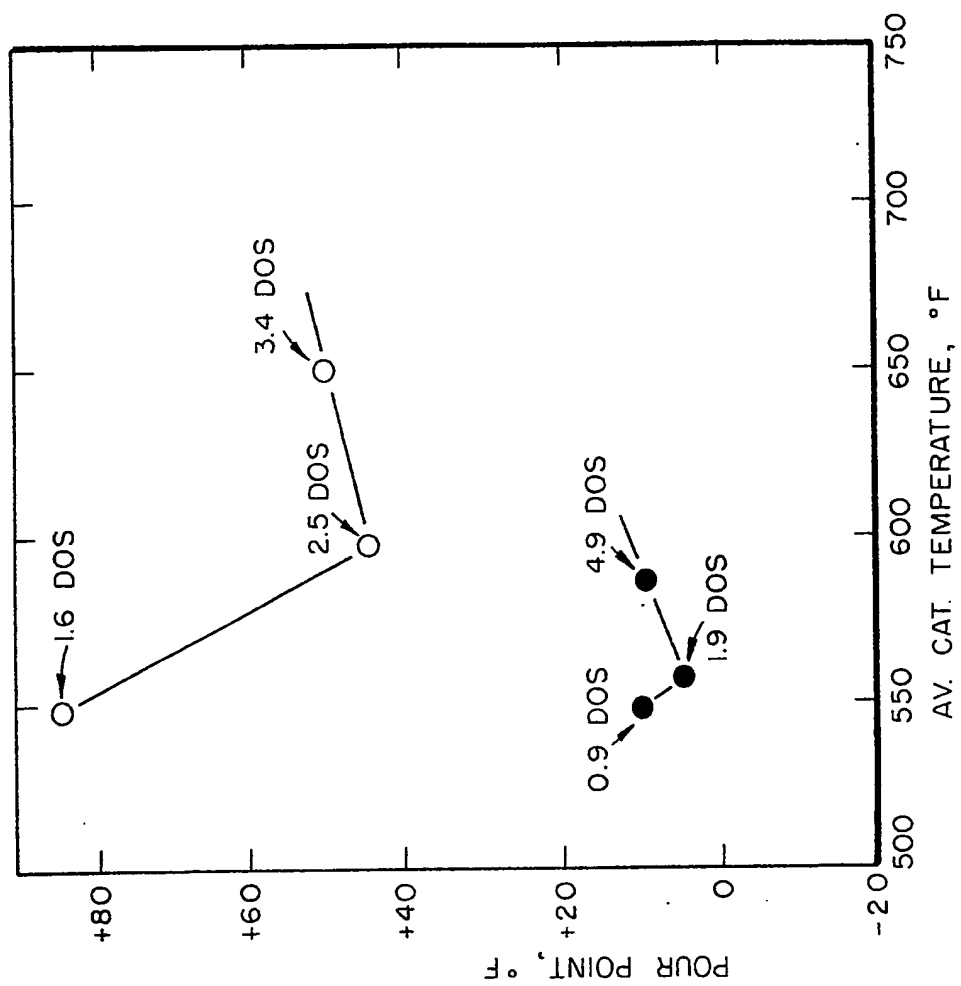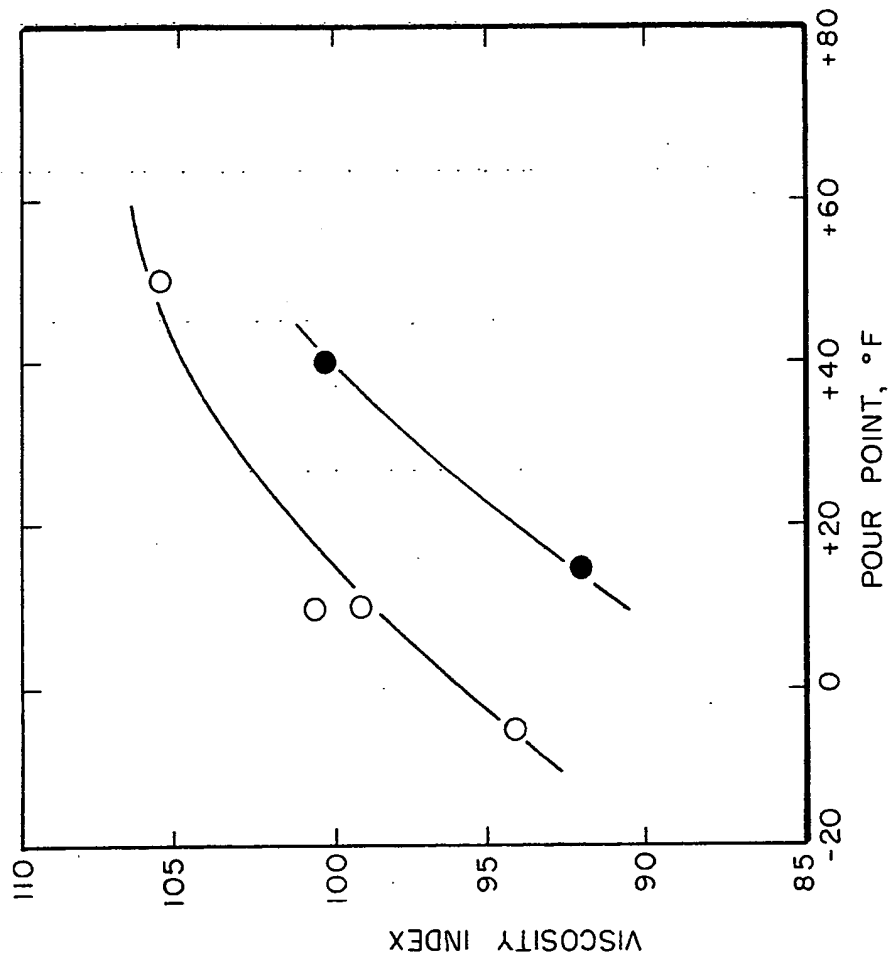
FIG.3

○ ZSM-23 ZEOLITE
(EXAMPLE 3)
● ZSM-5 ZEOLITE
(EXAMPLE 4)